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MAY 1966

Report No. IITRI-C6066-3
(Quarterly Progress Report)

A FEASIBILITY STUDY TO INCREASE
THE ACTIVITY OF OXIDES WITH OXYGEN
AND TO LOWER THE IGNITION TEMPERATURE
OF SLURRY METALS

Air Force Aero Propulsion Laboratory

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ABSTRACT

A FEASIBILITY STUDY TO INCREASE THE ACTIVITY OF OXIDES WITH OXYGEN AND TO LOWER THE IGNITION TEMPERATURE OF SLURRY METALS

The main objective of this reporting period was to commence with the investigation on the influence of doping and of pre-exposure to gamma ray radiation on the reversible oxidation-decomposition reactions of cobalt oxide, $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + 1/2 \text{O}_2$. The principal experimental techniques used were differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The results indicate that doping cobalt oxide with foreign cations can significantly alter its high temperature chemical reactivity characteristics. Li^+ ion is especially effective as a doping agent to decrease the decomposition reaction temperature and increase the reaction rate. In some cases such as where the oxide is doped with Li^+ or Ag^+ ions the oxidation or decomposition reaction appears to occur in two steps.

**A FEASIBILITY STUDY TO INCREASE THE ACTIVITY
OF OXIDES WITH OXYGEN AND TO LOWER THE IGNITION TEMPERATURE
OF SLURRY METALS**

PHASE I

SCOPE

The purpose of this phase of the program is to determine if it is possible to increase the rate of the solid state reversible oxidation-reduction reactions of cobalt oxide and of the palladium-palladium oxide system at elevated temperatures. The approaches are to dope the solid with selected altermvalent ionic impurities and to explore possible increases in reactivity due to the creation of lattice defects resulting from exposure to high energy radiation.

OBJECTIVES FOR THE REPORTING PERIOD

1. To decide on sample preparation as well as the cationic impurities to dope cobalt oxide and to decide upon the experimental procedures.
2. To prepare samples of doped and undoped cobalt oxide.
3. To commence with the experimental investigation on the effects of the doping of the oxide and exposure to gamma rays on the rates of the reversible decomposition-oxidation reactions of cobalt oxide.

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4. To initiate reactivity studies on palladium.

RESULTS DURING REPORTING PERIOD

1. Procedures for preparing doped and undoped samples have been decided upon as well as the experimental methods for studying the chemical reactivity of the samples with respect to decomposition and oxidation. The details are discussed below.

2. Preparation of Samples

Preparation of the Doped Materials

Solutions of cobaltous nitrate with the nitrates of the doping ions were mixed in the proper mole ratio (1% of doping ion with respect to cobalt) and the mixture dried in an oven at 110°C. After drying, the mixed nitrates were stored in a dessicator for further use in the DTA and TGA experiments.

The following cationic impurities were used to dope the cobalt oxide: Li^+ ion, Pb^{++} ion, Fe^{+++} ion, Cr^{+++} ion, Be^{++} ion, Zr^{++++} ion and Ti^{++++} ion. All of the nitrates used in the sample preparations were reagent grade and had the following purity specifications:

- (a) Cobaltous nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Fisher, less than 0.3% impurities
- (b) Silver nitrate, AgNO_3 , B+A, Code 2179, less than 0.04% impurities
- (c) Lead nitrate, $\text{Pb}(\text{NO}_3)_2$, B+A, Code 1838, Assay ($\text{Pb}(\text{NO}_3)_2$) minimum 99.5%

- (d) Lithium nitrate, LiNO_3 , Fisher, less than 0.2% impurities
- (e) Ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, B+A, Code 1739, minimum purity 99.0%
- (f) Chromium nitrate, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, B+A, Code 1578, minimum purity 98.5%
- (g) Zirconyl nitrate, $\text{ZrO}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$, Fisher, purity specifications unknown
- (h) Beryllium nitrate, $\text{Be}(\text{NO}_3)_2$, K+K, reagent grade, purity specifications unknown.
- (i) Titanium nitrate, $\text{Ti}(\text{NO}_3)_2$, K+K, reagent grade, purity specifications unknown.

The impurity ions were selected primarily on the basis of charge and size considerations. Ions having valencies ranging from +1 to +4 were selected since the nature of the defect structure of the oxide will depend on whether the valency of the impurity ion is greater or less than of the cation in the host lattice. Ions of similar size to that of Co^{++} ions, the host lattice cation, this represents the best condition for the incorporation of the impurity ions with substitutional lattice positions. The introduction of ions having a lower valency than the host cation may be expected to increase the concentration of positive holes in the lattice and/or decrease the concentration of cation vacancies or increase the concentration of anion vacancies.

Preparation of Irradiated Cobalt Oxide

Cobalt oxide, Co_3O_4 , B+A, Code 1590 assay (as Co) min. 70% was used for the irradiation experiments. A sample of the oxide was subjected to γ -irradiation from a Co^{60} -source of a total dose of 1.7×10^7 rads. DTA runs were performed immediately after irradiation as well as over longer time intervals and the results compared to the unirradiated material. Irradiation may be expected to result in a decrease in the positive hole concentration and an increase in the concentration of interstitial cobalt ions.

3. Experimental Studies on the Effects of Doping and Radiation

Differential Thermal Analysis (DTA)

Differential thermal analysis is an especially valuable method to investigate and compare the energetics of reacting systems under dynamical conditions. One of the major reasons for this is that in a single experimental run one can cyclically observe the decomposition-oxidation reaction by first heating to elevated temperature and then cooling. The sample under investigation is placed into a sample holder which is heated and cooled at a constant, predetermined heating rate. The temperature difference, ΔT , between the sample and an inert reference material such as ignited Al_2O_3 , which are heated simultaneously, is plotted as a function of reference temperature or time. Reactions which involve the absorption of heat such as decomposition are indicated by an endothermal band in the

downward direction and reactions in which heat is liberated such as oxidation are indicated by exothermal bands in the upward direction. During the initial heating cycle the cobalt nitrate is first decomposed to form Co_3O_4 which at higher temperatures decomposes to CoO . On cooling the CoO reacts with oxygen to form Co_3O_4 . The heating-cooling cycle may be repeated in a single experiment as many times as considered desirable. After the first cycle the endotherm for the decomposition of the nitrate will no longer appear.

For recording of the temperatures Pt versus Pt 10% Rh thermocouples were used. ΔT is plotted as a function of time simultaneously with the temperature. Figure 1 exhibits the Stone DTA/TGA equipment which was used in this study. Gas inlets into the sample holder are connected via a flowmeter to a gas cylinder to provide for standardized gas flow. Except for one experiment which was run in pure oxygen, all experiments were run in air. All heating rates employed were nominally $20^\circ\text{C}/\text{min}$. Figure 2 shows the Stone TGA-balance which is also regulated by the controller shown in Figure 1. With the TGA balance the weight loss as well as the differential weight loss can be recorded simultaneously as a function of temperature and time.

In Figure 3 the DTA curves of cobaltous nitrate carried out in an air and later in an oxygen atmosphere are shown. The initial portion at lower temperatures involves the release of water and the oxidation of the nitrate to the oxide, Co_3O_4 . An endotherm appears between 900 and 1000°C which is due to the

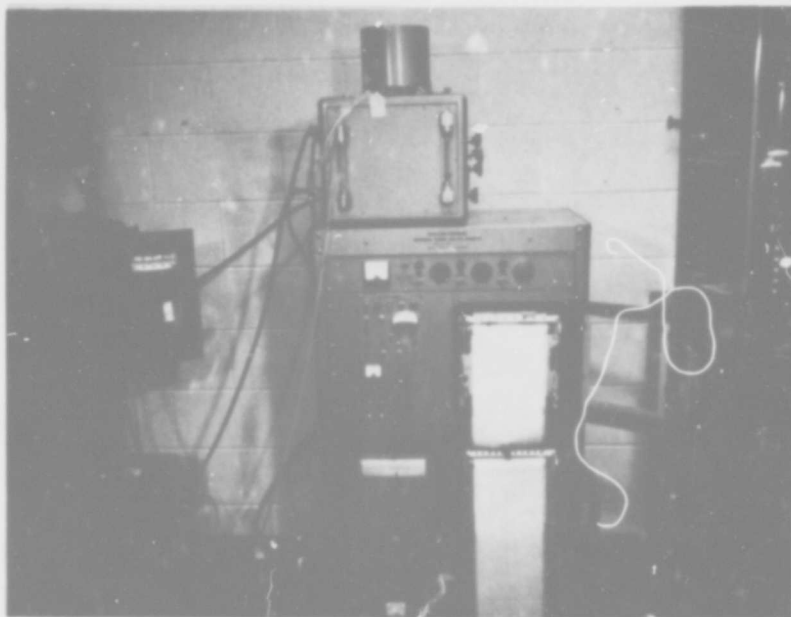


Fig. 1. THE STONE DTA APPARATUS AND CONTROLLER

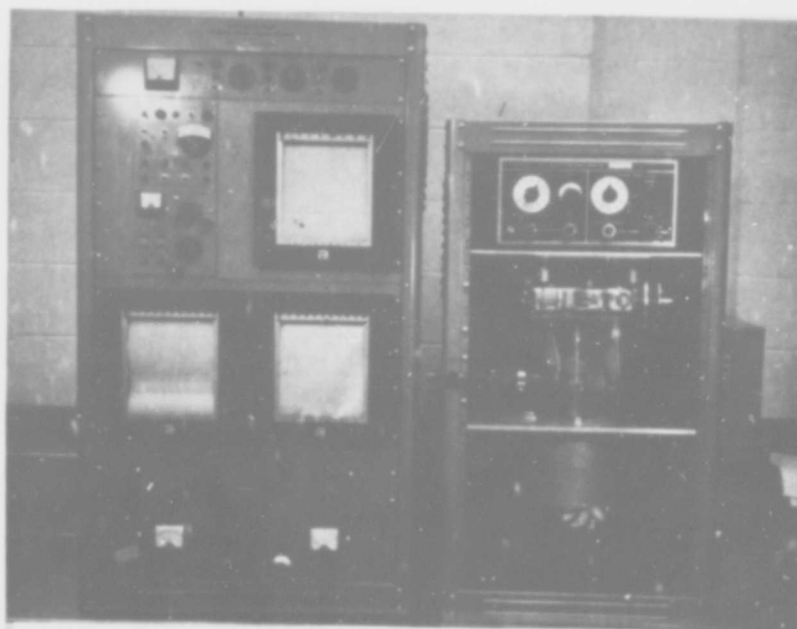


Fig. 2. THE STONE TGA APPARATUS

Figure 3

**DIFFERENTIAL THERMAL ANALYSIS OF THE SYSTEM
 $\text{Co}_3\text{O}_4/\text{CoO}$**

Sample: - $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Sample Size: - Approx. 5 mg
Atmosphere: - O_2 and air
Flow rate: - Approx. 40 ml/min
Heating rate: - $18.6^\circ/\text{min}$

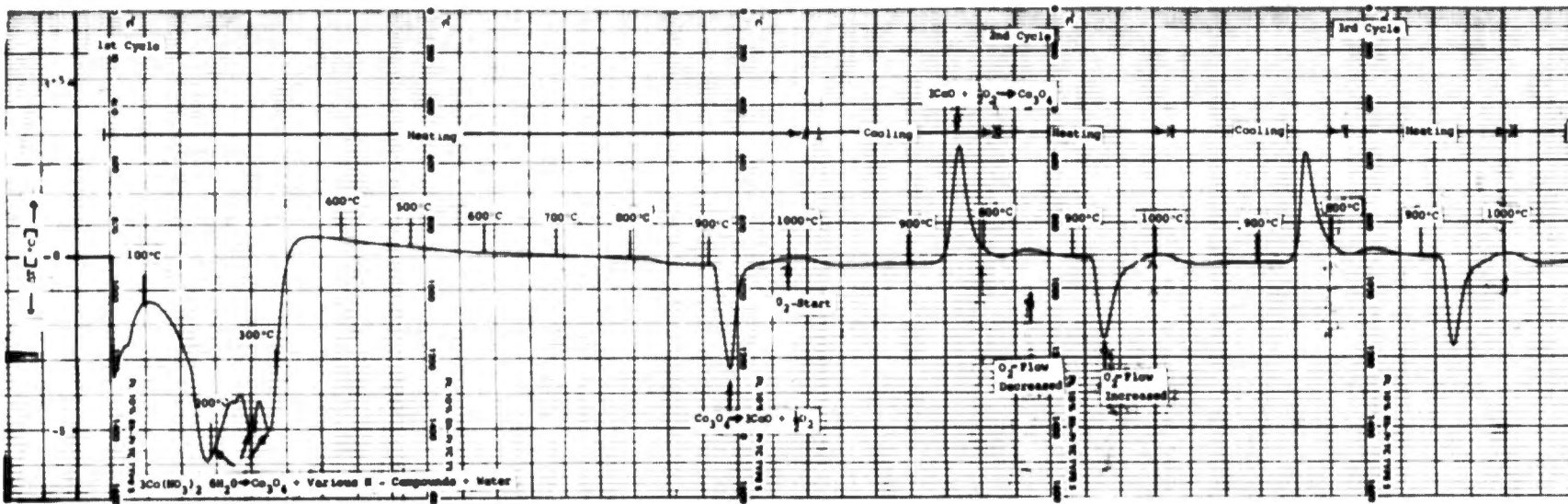
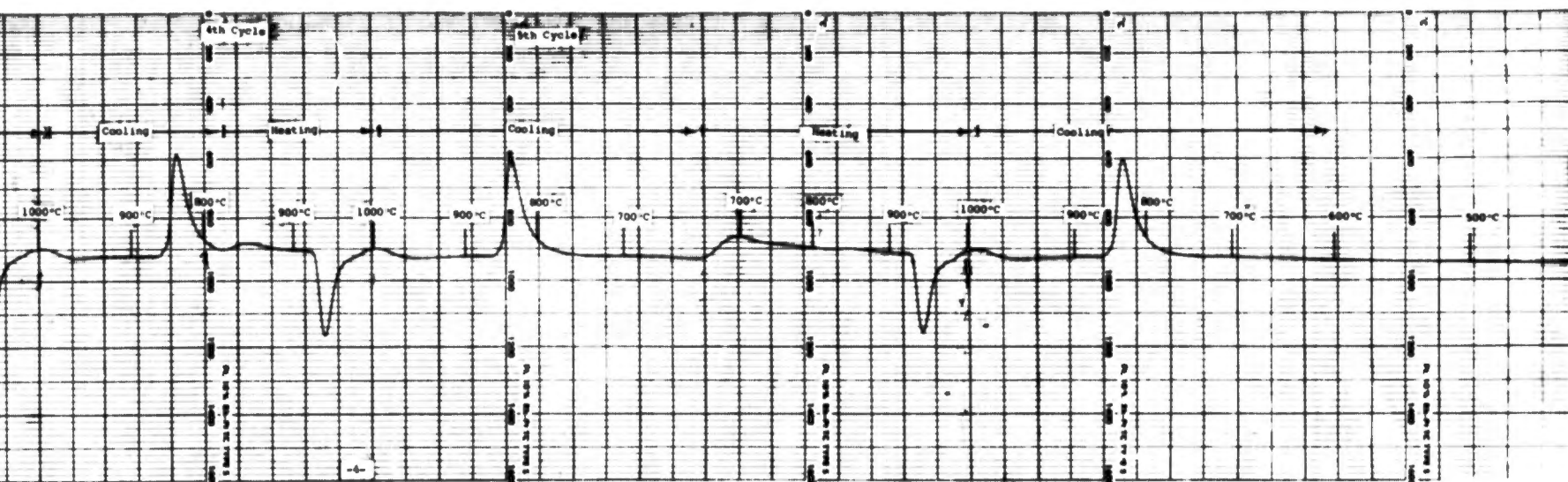


Fig. 3. DIFFERENTIAL THERMAL ANALYSIS

A



THERMAL ANALYSIS OF THE SYSTEM $\text{Co}_3\text{O}_4/\text{CoO}$

B

release of oxygen. The decomposition reaction may be expressed by the following equation:



On cooling the oxygen is reversibly picked up again between 900 and 800°C by the cobaltous oxide, $3\text{CoO} + 1/2 \text{O}_2 \rightarrow \text{Co}_3\text{O}_4$. Excellent reversibility is reflected in several heating and cooling cycles, where the position and the appearance of the peaks remain comparable.

In Figures 4 and 5 the endothermal and exothermal peaks and valleys, respectively, are compared for various doped cobalt oxides. These runs were all done in a flow of dry air at a flow rate of 40 ml/min. The oxides were obtained by heating the doped nitrates in the DTA furnace, where conversion to the oxides occurs at lower temperatures. The curves show that in a number of cases doping has a pronounced effect on the reaction temperatures and on the reaction rates of the reversible oxidation-decomposition reaction. The temperature of decomposition is in most cases (including the undoped material) slightly above 900°C. With the lithium-doped cobalt oxide, however, decomposition starts significantly below 900°C. It appears that in this case the reaction takes place in two definite steps. The separation of the decomposition reaction into two stages of reaction becomes increasingly pronounced during the second and third cycle. Preliminary TGA-data on the lithium doped sample confirms the two-stage decomposition reaction. The two-step decomposition process is also seen to occur after the first

Figure 4

THE INFLUENCE OF DOPING ON DTA CURVES
OF THE REACTION $\text{Co}_3\text{O}_4 = 3\text{CoO} + 1/2 \text{O}_2$

Sample: - Undoped Co_3O_4
Doped with 1% Fe^{+++}
Doped with 1% Cr^{+++}
Doped with 1% Zr^{++++}
Doped with 1% Li^+

Sample Size: - Approx. 5 mg

Atmosphere: - Dry air

Flow rate: - 40 ml/min

Heating rate: - 18.6°/min

Fig. 4. THE INFLUENCE OF DOPING ON DTA CURVES OF THE REACTION $\text{CaO} \rightleftharpoons \text{CaO} + \text{V}_2\text{O}_5$

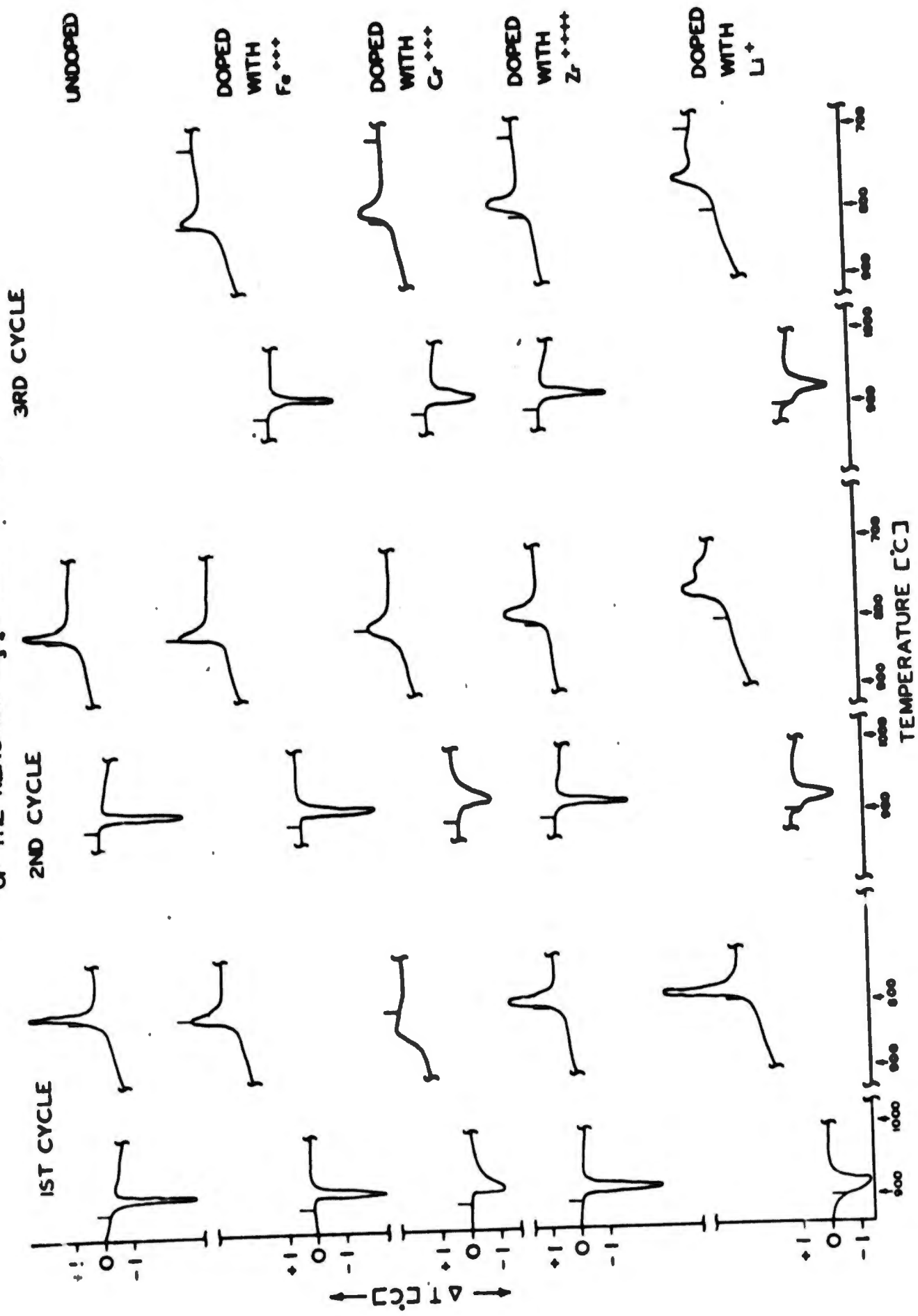
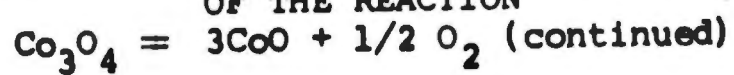


Figure 5

THE INFLUENCE OF DOPING ON DTA CURVES
OF THE REACTION



Sample: - Undoped Co_3O_4
 - Doped with 1% Pb^{++}
 - Doped with 1% Ag

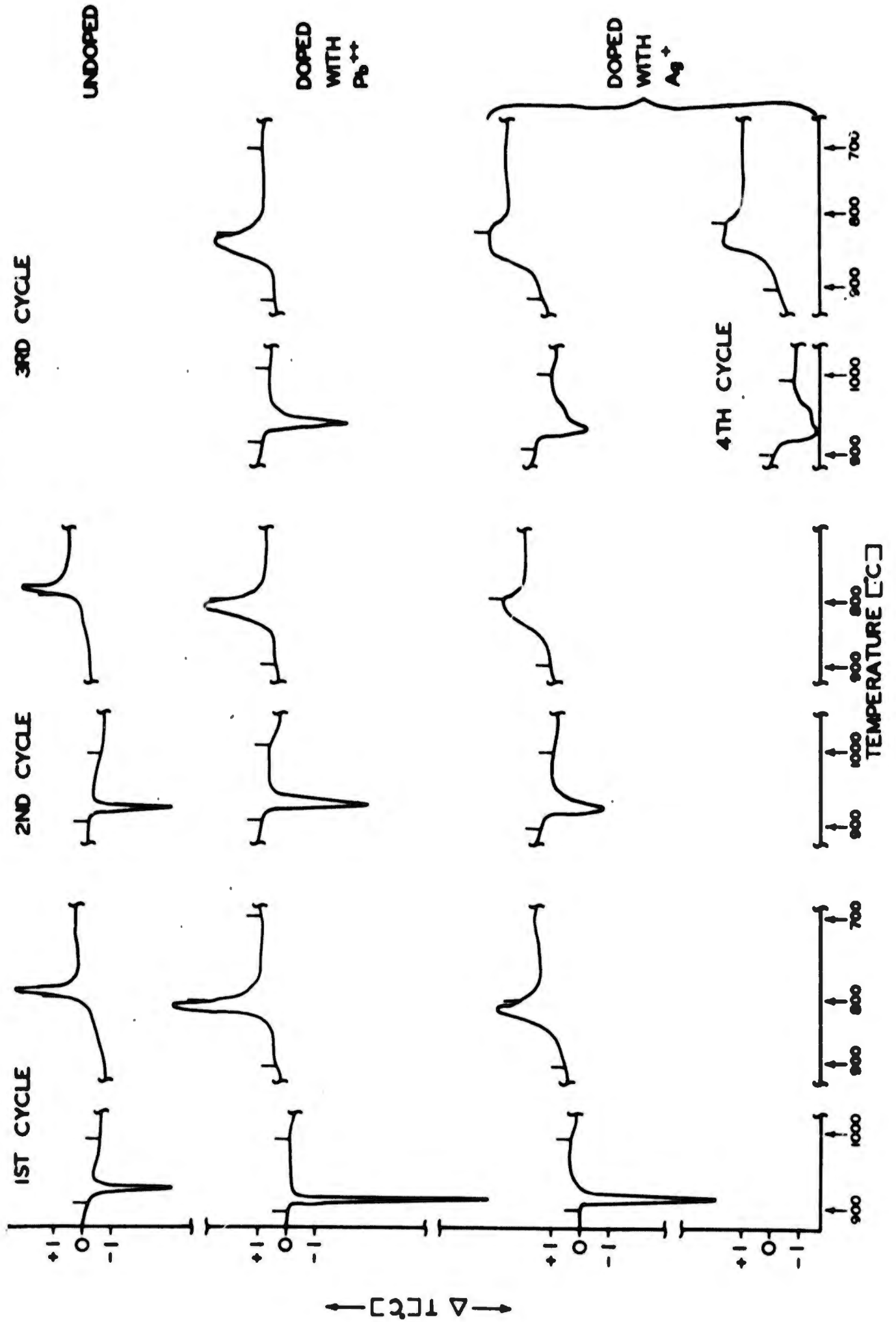
Sample Size: - Approx. 5 mg

Atmosphere: - Dry air

Flow rate: - 40 ml/min

Heating rate: - 18.6°/min

Fig. 5. THE INFLUENCE OF DOPING ON DTA CURVES OF THE REACTION
 $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + 1/2 \text{O}_2$ (continued)



cycle during the oxidation reaction between 800° and 700°C.

In some cases, such as with chromium ion as the doping impurity, the decomposition reaction of Co_3O_4 during the first cooling half-cycle occurs at a higher temperature than it does for the pure oxide. While, generally the oxidation reaction takes place between 800° and 700°C, the reaction of the Cr^{+++} ion doped oxide begins slightly below 900°C. During subsequent cycles, however, the oxidation exotherm shifts back to lower temperatures between 800° and 700°C. With the silver-doped cobalt oxide the oxidation exotherm stays between 900° and 800°C even during at least 4 cycles without shifting. Both the endotherm for decomposition as well as the oxidation exotherm split into two. With the lead-doped material a similar stabilization of the oxidation reaction as with silver is apparent. (The oxidation peak is between 900° and 800°C as compared to that of pure cobalt oxide between 800° and 700°C.)

Differential Thermal Analysis of Irradiated Cobalt Oxide

In Figure 6 the DTA characteristics of irradiated as compared to unirradiated cobalt oxides are shown. The drastic change in the curve shape of the oxidation exotherm between 800° and 700°C was tentatively interpreted as due to the γ -irradiation. The TGA curve of the irradiated material did not, however, appear to differ significantly from that of the unirradiated cobalt oxide.

Figure 6

THE INFLUENCE OF GAMMA-IRRADIATION
ON THE DTA CURVES OF COBALT OXIDE

Sample: - Co_3O_4 unirradiated
 - Co_3O_4 immediately after
 irradiation
 - Co_3O_4 three days after
 irradiation

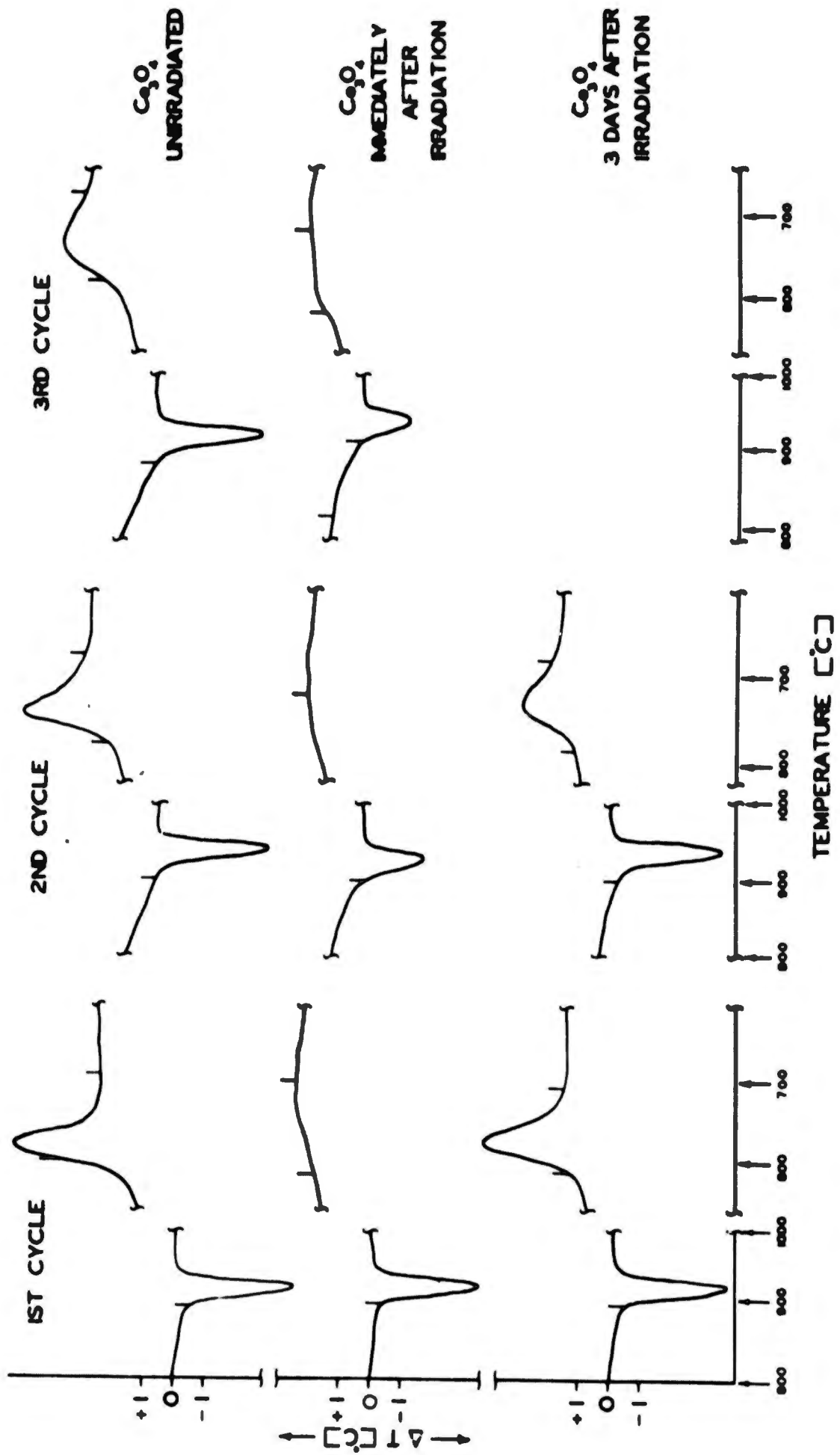
Sample Size: - Approx. 5 mg

Atmosphere: - Dry air

Flow rate: - 40 ml/min

Heating rate: - 18.6°/min

Fig. 6. THE INFLUENCE OF GAMMA-IRRADIATION ON THE DTA CURVES OF COBALT OXIDE



From further studies it was found that in the original DTA run with the irradiated Co_3O_4 (second curve in Figure 6), the heating was carried out to temperatures higher than 1100°C . The differential thermal analysis of an unirradiated sample, where the sample was also heated above 1100°C , yielded a similar broad DTA oxidation exotherm as in the case of the irradiated material (second curve). It is probable that the heating above 1100°C effects the structure of the oxide which causes the subsequent solid state reactions to occur over a much larger temperature range than in samples which are heated just slightly above the endotherm for decomposition. X-ray analysis will be conducted to confirm these high temperature structural effects.

The Thermogravimetical Analysis of Doped and Pure Cobalt Oxides

In Figure 7, TGA traces are shown together with their corresponding differential TGA curves. The oxidation process of the lithium-doped sample after the first cycle occurs in two distinct stages which corresponds to the observations from the DTA experiments.

It is quite interesting that the data thus far indicate that doping with a lower valent cation such as Li^+ ion appears to have the effect of increasing the chemical reactivity of

Figure 7

THERMOGRAVIMETRIC ANALYSIS OF COBALT OXIDE
UNDOPED AND DOPED WITH LITHIUM

Sample: - $\text{Co}(\text{NO}_3)_2$
 $\text{Co}(\text{NO}_3)_2$ doped 1% Li

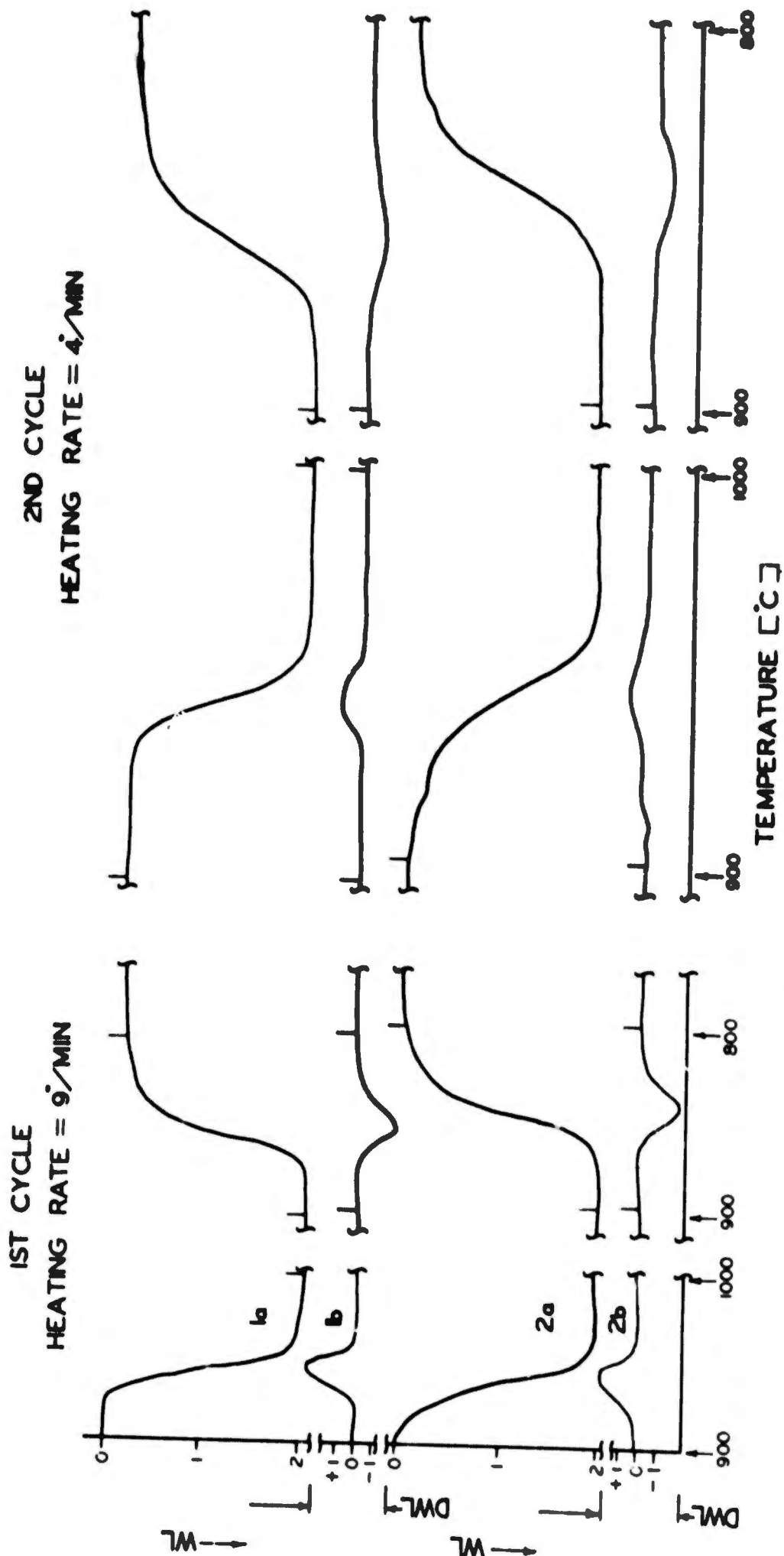
Sample Size: - Approx. 95 mg

Atmosphere: - In air

Flow rate: - No flow

Heating rate: - $9^\circ/\text{min}$ and $4^\circ/\text{min}$

Fig. 7. THERMOGRAVIMETRIC ANALYSIS OF COBALT OXIDE
 UNDOPED AND DOPED WITH LITHIUM



- 1a TGA CURVE OF COBALT OXIDE
- 1b DIFFERENTIAL TGA [DTGA] CURVE OF UNDOPED COBALT OXIDE
- 2a TGA CURVE OF COBALT OXIDE DOPED WITH LITHIUM
- 2b DTGA CURVE OF COBALT OXIDE DOPED WITH LITHIUM
- WL WEIGHT LOSS [IN MG]
- DWL DIFFERENTIAL WEIGHT LOSS [ARBITRARY SCALE]

cobalt oxide with respect to thermal decomposition and rate of oxidation, whereas in the case of higher valent ions such as Fe^{+++} and Cr^{+++} the reverse effect occurs; the reactivity of the oxide is decreased. These results seem to indicate that the diffusion of cations is not rate controlling but that the chemisorption and dissociation of oxygen on the surface of the oxide may be of considerable importance. The reason for this is that if diffusion were rate controlling, then one would expect that the reaction of cation vacancies, which enhances the diffusion process, will increase the reaction rate. However, the reverse is observed, the most reactive oxide is the Li^+ ion doped sample which should have the lowest concentration of cation vacancies, and the lowest reactivity occurs with the Fe^{+++} and Cr^{+++} doped samples which should have the highest concentration of cation vacancies. It therefore appears that increasing the positive hole concentration in the valance band of the oxide may play an important role in controlling the reaction rates of the oxide since doping with Li^+ ions may cause an increase in the positive hole concentration of the oxide, whereas doping with ions of +3 or higher valence will reduce the positive hole concentrations. If this is true then the electron transfer reactions between the solid and oxygen on the surface of the solid will be the important factor. Another possibility which must not be ruled out without evidence is that there is an increase in anion vacancies due to doping with Li^+ ion. This, of course, will favor the

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diffusion process. Obviously, further work is required to settle these questions.

It may also be noted that the shapes of the peaks appear to change for the doped samples as the number of heating cycles is increased. This indicates that the impurity ions may be migrating to the most energetically favorable positions in the lattice. Lower or less pronounced endotherms indicate that the reaction rate is either occurring over a larger temperature range or that the reaction rate is decreased if the temperatures of the DTA peaks are relatively unchanged.

4. Samples of palladium were ordered for the study of the chemical reactivity of Pd with respect to its reactions with oxygen and of the thermal decomposition of the resulting oxide. Many of the procedures used for the investigation of increasing the reactivity of boron will also be used in this phase of the research.

OBJECTIVES FOR THE NEXT REPORTING PERIOD

1. The experiments on the effects of doping and exposure to gamma and neutron radiation on the chemical reactivity of cobalt oxide will continue. This will include the study of the effects of Be^{++} and Sc^{+++} ion impurities. To initiate studies of the effects of doping with anionic impurities such as I^- and F^- ions.

2. The investigation of additional doping procedures will be initiated including heating the oxide in alkali metal vapors.
3. Kinetic and x-ray studies will be initiated. The IBM 7094 computer may be utilized for determining the rate constants if time permits.
4. To begin experimental work on the oxidation of palladium.

Respectfully submitted,

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PHASE II

SCOPE

To determine if it is possible to increase the rate of combustion of boron powder fuel by doping with selected impurities and by exposure to high energy radiation.

OBJECTIVES FOR REPORTING PERIOD

1. To decide on experimental approach and to obtain reagents.
2. To initiate the experimental work with commercial grade amorphous boron powder in which the effects of selected fluorides and silicofluoride impurities on the combustion rate of boron would be investigated.
3. To carry out combustion experiments on special fine particle boron supplied by Air Force Aero Propulsion Laboratory.
4. To determine particle size distribution of the boron powder under investigation.

RESULTS FOR REPORTING PERIOD

1. Amorphous boron powder 99.5% pure, was obtained from the Fisher Scientific Company. This sample will be used in all the experimental work. Samples from Air Force Aero Propulsion Laboratory will also be used when received. The average particle size of this sample will be determined during the program. All of the reagents to be used in this program have also been ordered.

Procedures for the DTA experiments have been optimized. The DTA apparatus decided upon essentially consists of a crucible furnace, a nichrome metal block which is placed in the furnace, a temperature program controller and an X-Y recorder. Three holes are drilled into the nichrome block. Two of these holes are used for the sample and reference materials, which are placed in pyrex test tubes. The third hole is located on the outer edge of the block where the thermocouple used to monitor heating rate is placed. Twenty eight gauge chromel-alumel thermocouples are used. The thermocouple wires in the sample and reference vessels are spread apart so that they hug the bottom part of the test tubes. For controlled atmospheres, the desired gases are admitted into the sample and reference tubes simultaneously at known flow rates. The experiments involve increasing the furnace temperature of the block containing the sample and reference materials, from room temperature to approximately 750°C at the rate of 10°C/min. Simultaneously the differential temperature between the sample and reference material is recorded on the X-Y recorder as a function of reference temperature. The finalized procedure arrived at involves using 125 mg of boron and 15 mg of fluoride impurity.

2. Initial work prior to receiving the 99.5% impurity sample was carried out on boron powder having a purity of 85-88 per cent. Three experiments were conducted with the following

dopants: lead fluoride, aluminum fluoride, and platinum powder. In each case 100 mg of boron powder was intimately mixed with 25 weight per cent of impurity. The results which are shown in Figure 8 demonstrate that lead fluoride has a very profound effect in increasing the rate of combustion of boron in air. The temperature at which rapid reaction occurred in the presence of lead fluoride was approximately 130°C lower than in the case of the boron alone. Aluminum fluoride and platinum did not appear to have significant effects in air. It should be kept in mind that these experiments were done, however, with relatively impure boron in order to initiate the program and establish some of the experimental parameters prior to the receipt of the purer sample.

Based on this work it was decided that in all subsequent work the 99.5% amorphous boron sample would be used and the doping ingredient would be present in an amount corresponding to 12 weight per cent of the quantity of boron. In terms of mole percent of impurity, lead fluoride for example, this represents less than 0.4% which should be negligible in terms of dilution. On a volume basis, the lead fluoride in the amount used contributes only approximately 3% to the total volume of the powdered mixture.

Experiments with the new 99.5% boron sample were conducted in oxygen at a flow rate of 300 ml/min. The DTA curves are shown in Figure 9. At the reaction temperatures there is a sharp exothermal rise followed by rapid decay after completion

Figure 8

DIFFERENTIAL THERMAL ANALYSIS CURVES

Material: A. Lower Curve - 100 mg
Amorphous Boron 85-88%

B. Upper Curve - 125 mg
Amorphous Boron 85-88%
with 25 mg Pb_2

Atmosphere: Air

Gas Flow Rate: Zero

Pressure: 1 Atmosphere

Equipment: Freeman DTA Setup

Heating Rate: $10^{\circ}C/min$

Initial Temperatures: $25^{\circ}C$

Final Temperatures: $715^{\circ}C$

X axis = 4.1 mv/in.

Y axis = 2 mv/in.

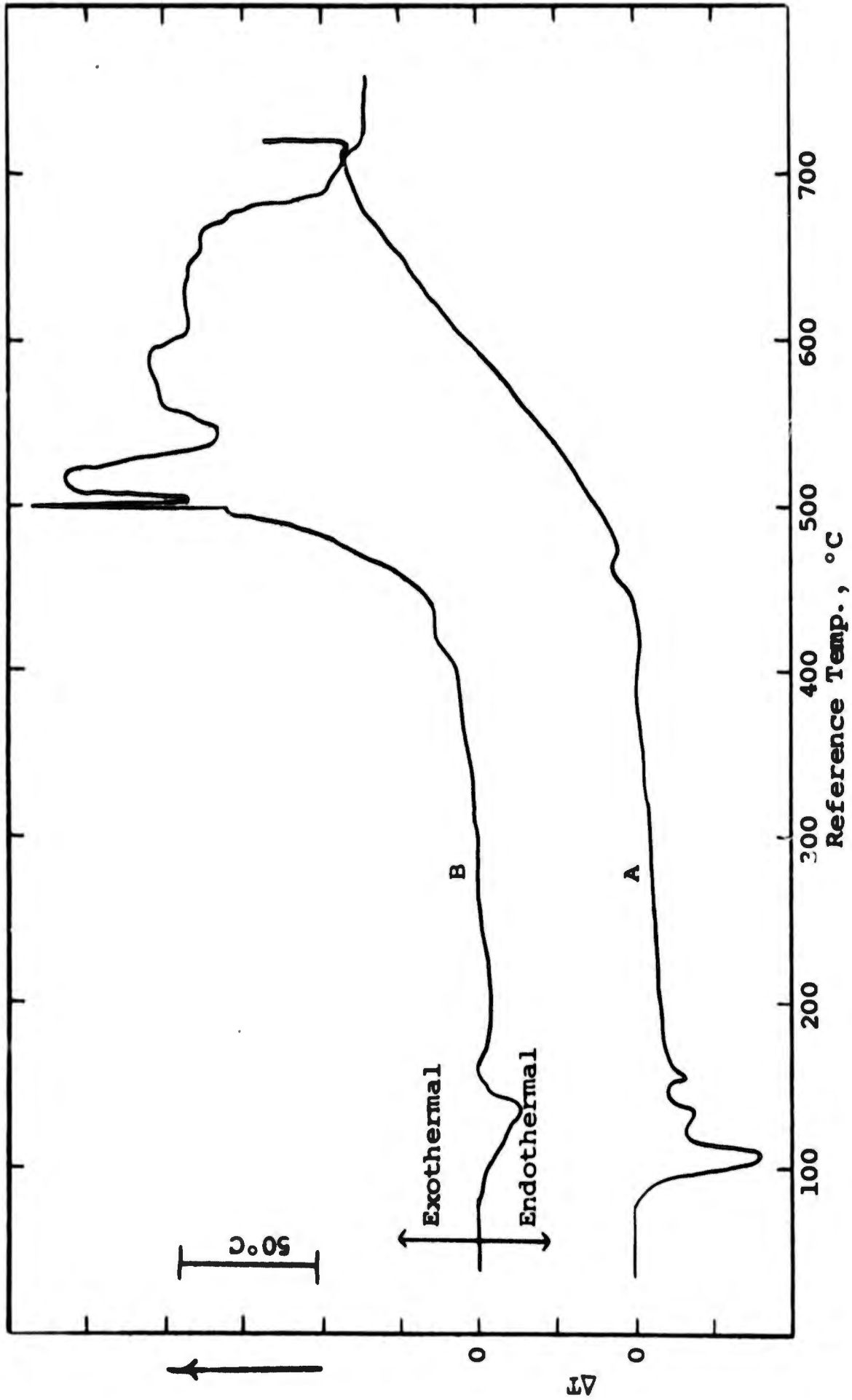


Figure 8
DIFFERENTIAL THERMAL ANALYSIS CURVES

Figure 9

DIFFERENTIAL THERMAL ANALYSIS CURVES

Material: A. Lower Curve - 125 mg
Amorphous Boron 99%+
B. Upper Curve - 125 mg
Amorphous Boron 99%
with 15 mg PbF_2 (powder)

Atmosphere: Oxygen

Gas Flow Rate: 300 ml/min

Pressure: 1 Atmosphere

Equipment: Freeman DTA Setup

Heating Rate: 10°C/min

Initial Temperature: 25°C

Final Temperature: 715°C

X axis = 4.1 mv/in.

Y axis = 2 mv/in.

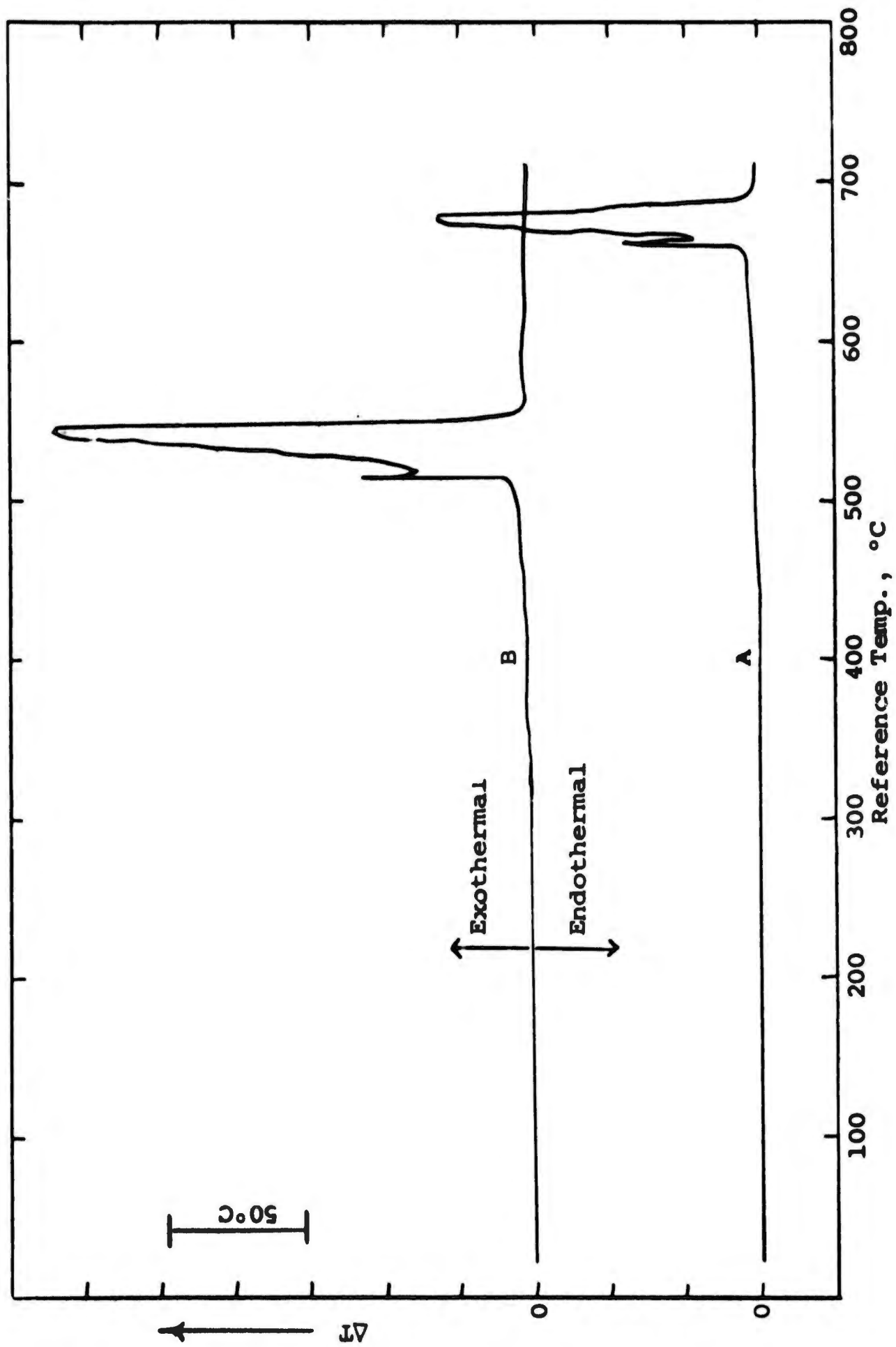


Figure 9
DIFFERENTIAL THERMAL ANALYSIS CURVES

of reaction. This results in a well defined exothermal band which represents the combustion of boron. During the exotherm, the boron has green then red glow due to ignition. In the presence of lead fluoride there is a decrease of 130°C in the temperature at which boron ignites. In addition to this decrease in ignition temperature, another interesting observation was made indicating the heat evolved during this reaction in the presence of lead fluoride may be as much as 2X that in the absence of lead fluoride. This is indicated from the areas under the DTA bands which are proportional to the heat of reaction. If the reaction were complete, theoretically there could be no increase in the heat of reaction. These results may therefore indicate that the boron did not undergo complete oxidation. However, in the presence of lead fluoride the reaction went considerably further to completion. It may be said with certainty that the rate of combustion of boron and ignitibility may be very markedly increased by doping with lead fluoride. As a result one may also expect an increase in combustion efficiency.

It was shown in previous work by Freeman that the complexes $\text{AlF}_3 \cdot \text{KF}$ and $\text{AlF}_3 \cdot 3\text{KF}$ have an appreciable effect on the combustion of aluminum. For this reason these complexes were prepared and their effect on the combustion of boron was determined.

The complex was formed during a differential thermal analysis experiment with the reactants aluminum fluoride and potassium fluoride which were intimately mixed. The DTA curve for this reaction is shown in Figure 10. The endotherm is due to the melting of the complexed aluminum fluoride-potassium fluoride. This is confirmed in the cooling curve, which shows an exotherm corresponding to the solidification of the melt. The complex is distinctly salmon pink.

Figure 11 shows the profound effect that the complex has on the combustion rate of boron. The figure demonstrates the effect of aluminum fluoride alone versus that of the complex. It is clear that although aluminum fluoride does not have an appreciable effect, the complex has a marked effect. Furthermore, it appears that the aluminum fluoride complex may be somewhat more effective than lead fluoride in increasing the rate of combustion, although the temperature differences are rather small.

Experiments using zinc silicofluoride hexahydrate as a dopant showed an appreciable difference in the peak height but not in the ignition temperature in comparison with the material that was not doped.

3. The results of the thermoanalysis experiment on the combustion of the special purity divided boron having a particle size range of from 100 to 1000 Å are shown in Figure 12. Two experiments were carried out thus far. The first experiment indicated that the sample ignited in oxygen at 440°C, however,

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Figure 10

DIFFERENTIAL THERMAL ANALYSIS CURVE

Material: Three parts by weight KF
One part by weight $\text{Al}_2\text{F}_6 \cdot \text{XH}_2\text{O}$
Lower curve represents heating curve
Upper curve represents cooling curve

Atmosphere: Argon

Gas Flow Rate: 300 ml/min

Pressure: 1 atmosphere

Equipment: Freeman DTA Setup

Heating Rate: $10^\circ\text{C}/\text{min}$

Initial Temperature: 25°C

Maximum Temperature: 725°C

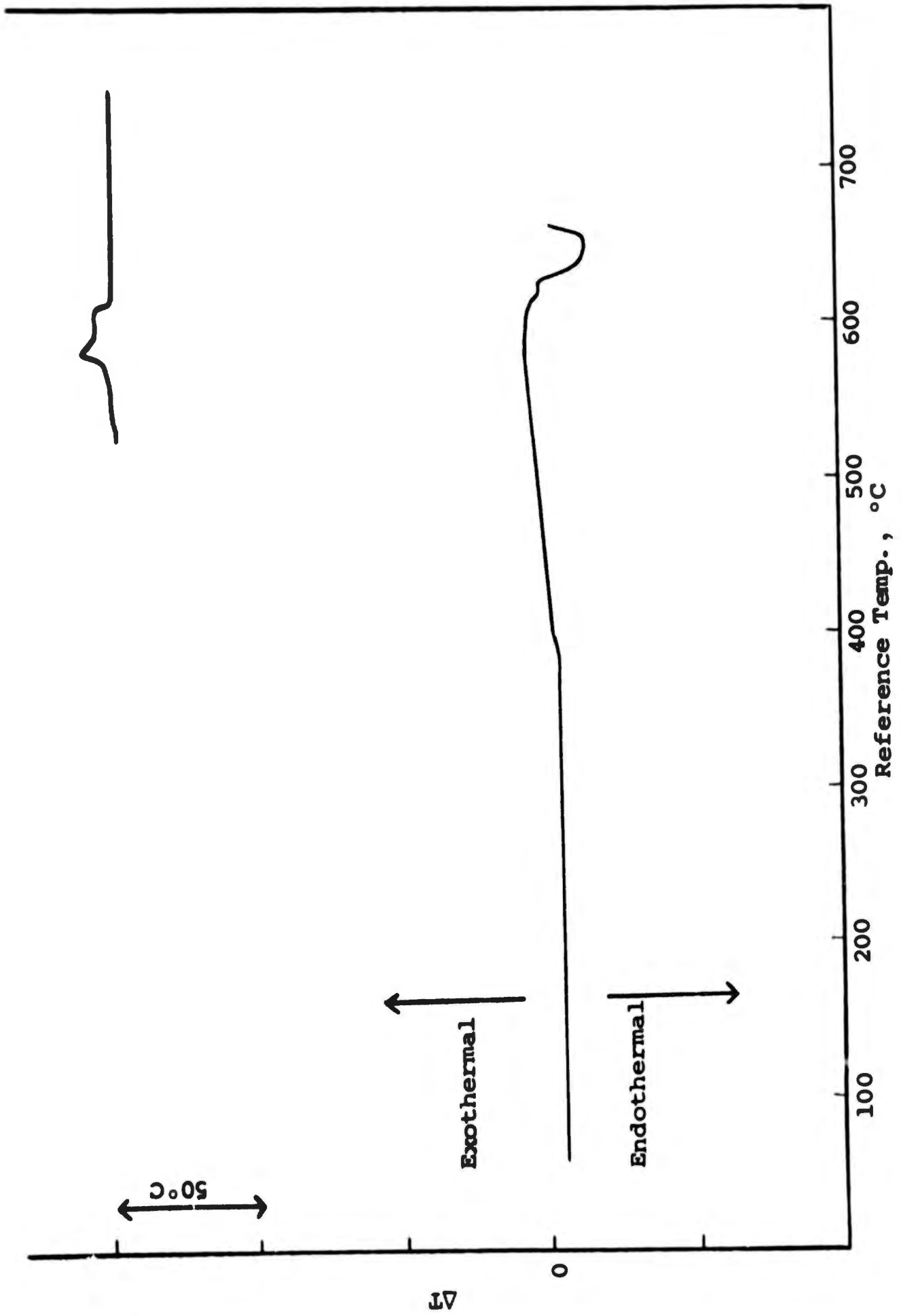


Figure 10
DIFFERENTIAL THERMAL ANALYSIS CURVES

Figure 11

DIFFERENTIAL THERMAL ANALYSIS CURVE

Material:	Curve A - Amorphous Boron 99.5% doped with lead fluoride
	Curve B - Amorphous Boron 99.5% doped with aluminum fluoride
	Curve C - Amorphous Boron 99.5% doped with aluminum fluoride-potassium fluoride complex.
Atmosphere:	Oxygen
Gas flow rate:	300 ml/min
Pressure:	1 atmosphere
Equipment:	Freeman DTA setup
Heating rate:	10°C/min
Initial temperature:	25°C
Maximum temperature:	715°C

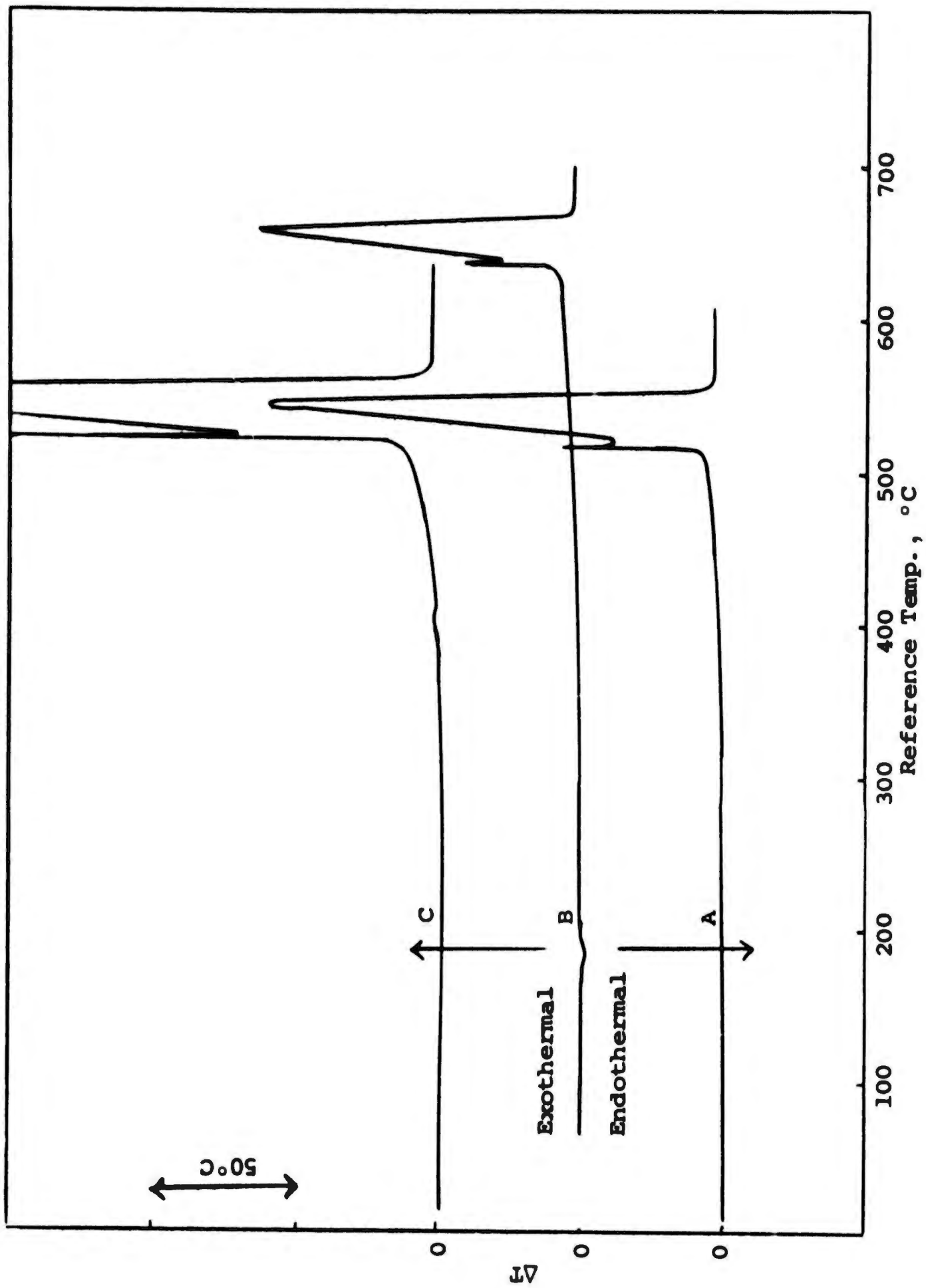


Figure 11
DIFFERENTIAL THERMAL ANALYSIS CURVES

Figure 12

DIFFERENTIAL THERMAL ANALYSIS CURVE

Material:	Curve A - Special fine particulate boron. DTA taken immediately after decapsulation.
	Curve B - Special fine particulate boron. DTA taken 36 hrs after decapsulation.
Atmosphere:	Oxygen
Gas flow rate:	300 ml/min
Pressure:	1 atmosphere
Equipment:	Freeman DTA setup
Initial temperature:	25°C
Maximum temperature:	550°C

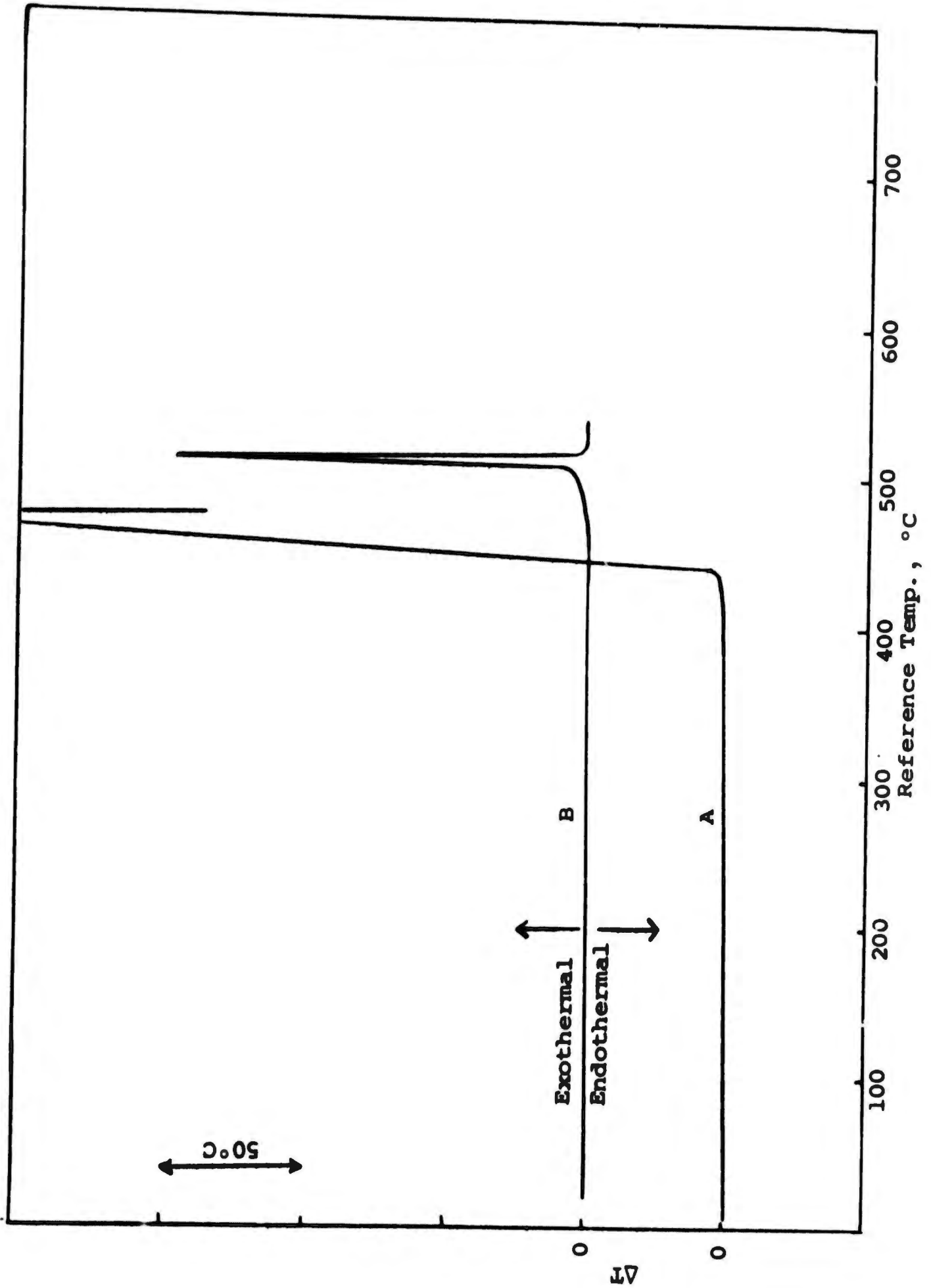


Figure 12

DIFFERENTIAL THERMAL ANALYSIS CURVES

the thermocouple malfunctioned when the sample ignited. A second experiment was conducted with ignition occurring at 510°C, which was 70°C higher than in the initial experiment. This apparent increase in ignition temperature may be interpreted as being due to some surface reaction of the boron after being taken out of its container and exposed to air. The material was originally packed under nitrogen.

The effects of the following fluorides and silico-fluorides on the combustion of the 99.5% pure amorphous boron powder were most recently considered.

- a. $(\text{NH}_4)_2\text{SiF}_6$
- b. $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$
- c. KF
- d. CaF_2
- e. NH_4F
- f. CaSiF_6
- g. $\text{Al}_2(\text{SiF}_6)_3$
- h. Na_2SiF_6

The two most interesting results were obtained with the potassium fluoride additive and with sodium silico-fluoride. The other materials did not show any apparent significant effects on the combustion rate of the boron.

The principal point of interest concerning the effect of potassium fluoride is that it appears to result in an extremely sharp ignition reaction at 590°C, whereas, in the other curves there appears to be a two-stage ignition process. The most

exciting result, however, was obtained with the sodium silico-fluoride additive, which was present in the ratio of 125 mg of boron to 15 mg of the additive. It appears from the results that sodium silico-fluoride is thus far the most effective material tried for increasing the ignitibility of boron. The exothermal combustion reaction begins at 495° and is comparable to the reactivity of the special finely divided boron powder. This result indicates the desirability of trying lithium silico-fluoride as an additive (see Figure 13). Table 1 summarizes all of the results obtained thus far.

4. The particle size distribution of the 99.5% Fisher Scientific amorphous boron sample used in this program has been determined and the results are given below. This work was carried out by Dr. B. Kaye of our Fine Particles Department.

Figure 13

DIFFERENTIAL THERMAL ANALYSIS CURVE

Material: Curve A - Amorphous Boron 99.5%
doped with potassium
fluoride

Curve B - Amorphous Boron 99.5%
doped with sodium
silico-fluoride

Atmosphere: Oxygen

Gas flow rate: 300 ml/min

Pressure: 1 atmosphere

Equipment: Freeman DTA setup

Heating rate: 10°C/min

Initial temperature: 25°C

Maximum temperature: 570°C

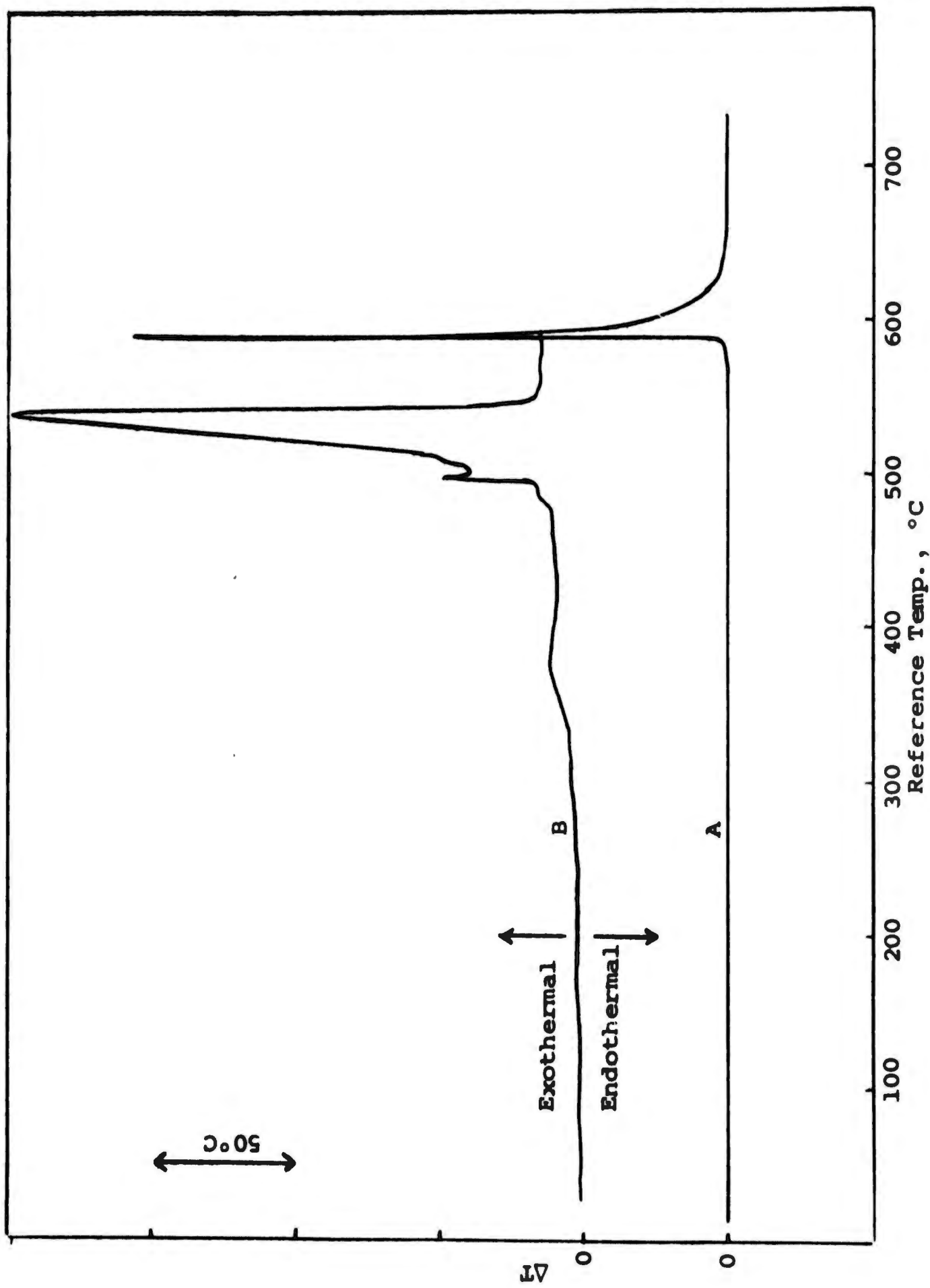


Figure 13

DIFFERENTIAL THERMAL ANALYSIS CURVES

Table 1

RESULTS OF BORON EXPERIMENTS
(Brief Summary)

<u>Material</u>	<u>Dopant</u>	<u>Temp. at which ignited (°C)</u>	<u>Comments</u>
99.5% B	none	660-700	
99.5% B	PbF ₂	515-550	Peak higher than boron.
85% B	Pt	652-685	Very similar to boron.
99.5% B	Al ₂ F ₆ ·xH ₂ O	640-670	Peak height similar to boron.
99.5% B	AlF ₃ ·KF	520-560	Peak appears to be somewhat larger than boron peak.
99.5% B	NH ₄ F	645-690	Little effect.
99.5% B	CaF ₂	610-660	Some effect.
99.5% B	KF	590-610	Different than others, peak very sharp, not at all broad.
99.5% B	ZnSiF ₆ ·6H ₂ O	655-685	Very similar to boron.
99.5% B	(NH ₄) ₂ SiF ₆	655-685	Little effect.
99.5%	MgSiF ₆ ·6H ₂ O	590-650	Intensity not changed from boron undoped.
99.5%	CaSiF ₆	610°C	Peak is similar to boron.
99.5%	Al ₂ (SiF ₆) ₃	610	Peak is small.
Irradiated B 99.5%	none	630-660	Little or no effect.
Special fine particle boron a. immediately after de- capsulation	none	a. 440—	Heat is very intense and broke thermo-couple.
b. 36 hours after decapsulation		b. 510	

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Table 1 (cont.)

<u>Material</u>	<u>Dopant</u>	<u>Temp. at which ignited (°C)</u>	<u>Comments</u>
Fine particle boron after standing in air.	none	510°	Peak was very sharp.
99.5% B	Na ₂ SiF ₆	490-535	Peak height high

All experiments were run as follows:

125 mg Boron, 300 ml/min O₂ flow, heating rate 10°C/min, 15 mg dopant, Cr-Al thermocouples used, 125 mg reference (Al₂O₃).

X-rays have been obtained for the unreacted boron and boron oxide. Weight measurements show that the efficiency of reaction is about 60% (if B₂O₃ is assumed to be the product).

Table 2

PARTICLE SIZE ANALYSIS OF BORON POWDER (99.5% Purity)

<u>Diameter, μ</u>	<u>Σ not greater than Diameter</u>
19.3	0
13.7	1.3
11.2	4.3
7.9	20.0
6.4	33.6
5.5	44.3
3.9	67.0
3.2	77.2
2.8	83.2
1.9	93.9
1.5	96.8
1.3	98.0
1.2	98.6
0.85	99.8
0.7 ₇	99.9
0.7 ₁	100.0

OBJECTIVES FOR NEXT REPORTING PERIOD

1. To carry out confirmatory experiments on the combustion of the finely divided boron powder.
2. To investigate the effects of lithium fluoride and lithium silicofluoride on the combustion of amorphous boron powder.
3. To conduct experiments to confirm the observed effects with boron powder samples supplied by Air Force Aero Propulsion Laboratory to initiate studies of the effects of doping with cesium.
4. To initiate studies in the hydrocarbon medium which is to be supplied by the Air Force Aero Propulsion Laboratory.

Respectfully submitted,

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